

The Fractionation of Lanolin With Urea¹

ABNER EISNER, WILFRED R. NOBLE, and JOHN T. SCANLAN,

Eastern Regional Research Laboratory,² Philadelphia, Pennsylvania

WOOL WAX, the secretion product of the sebaceous glands of the sheep, is a complex mixture of high molecular weight esters. A large number of acids and alcohols have been isolated (10, 2, 6, 3) from the saponification products of wool wax. Some of the alcohols are dihydric, and some of the acids are hydroxy acids. Consequently the possible number of ester and diester combinations is very large. However it has been demonstrated that many of the components of both alcohol fraction and the acid fraction form urea adducts (7, 8). Some of the esters present should also possess the necessary requirements to form adducts with urea, but statements that wool grease does not form an adduct with urea have appeared in the literature (9).

In the course of an investigation of the transesterification of lanolin with methyl acetate, the formation of urea adducts was used as a measure of the extent of the transesterification reaction. As a check on the validity of this procedure, a blank run was made on the original lanolin. It was found that by applying the method for making urea adducts to lanolin, a urea adduct can be made. The fraction forming the complex is about 6–8% of the original lanolin. In addition to the hard, nontacky wax fraction recovered from the separated urea complex, a fluid fraction and a sticky semisolid were also obtained. The latter two fractions were obtained by the solvent extraction of the nonadduct-forming material from urea adducts.

The fluid fraction, a viscous liquid at room temperature, amounts to about 71% of the original lanolin. The properties of this fraction indicate that it may have considerable practical utility. Its analysis shows it to be practically of the same composition as lanolin. This and the ease with which it can be handled make it potentially valuable for use in formulations in place of ordinary lanolin. Furthermore it has better solubility than unmodified lanolin. At 25°C. a 10% solution of the fluid fraction in mineral oil remains clear while a similar solution made from ordinary lanolin is cloudy. As in the case of lanolin, a further improvement in the fluid properties of the fraction can be obtained by acetylation (1).

In the production of the complexes, *i.e.*, when lanolin was treated with urea and methanol, the solution of any one component in any other was only partial, and the result was a physical mixture in the form of a stiff paste. In order to separate the complexes from the portion of lanolin which does not form a complex, it was necessary to extract the latter with a solvent. Ether was used because the solubility of urea in ether is slight; consequently the possibility of destroying the complexes during the extraction is lessened. The bulk of the extraction was carried out by slurring the mixture with cold ether and filtering. The filter cake was washed several times with cold ether. The batch-extraction did not remove all the noncomplex-forming material. Some of the nonad-

duct-forming material clung tenaciously to the complexes but could be recovered by extraction with ether in a Soxhlet apparatus. The three fractions thus obtained differ markedly in appearance. The noncomplex fraction most easily removed from the adducts was a viscous liquid. The second noncomplex fraction was a sticky semi-solid. The complex-forming fraction was a hard, white wax.

Experimental

Five hundred grams of U.S.P. lanolin were mixed with 1,500 ml. of methanol and 480 g. of urea while being heated on the steam bath. Heating was continued until sufficient methanol had boiled off to leave the mixture as a stiff paste. The mixture was then removed from the source of heat and stirred vigorously, using a mechanical stirrer, for 45 min. At the end of the stirring period the mixture was cooled to 2°C. and kept at this temperature over-night. Sufficient ether was added to form a thin slurry, and the resulting mixture was filtered. The material on the filter was washed with more cold ether. The ethereal filtrate and washings were combined, extracted with dilute HCl to remove any urea, and water-washed until neutral. The ether was then removed by distillation. The residue was a fluid product (Fraction I) amounting to 71% of the original lanolin. The filter cake was extracted with ether in a Soxhlet apparatus for 24 hr. The ether extract worked up in a manner similar to that described above, yielded a sticky, semi-solid material (Fraction II), amounting to 19% of the original lanolin. The ether-insoluble material, comprising the urea adducts, was decomposed by heating with dilute hydrochloric acid. The complex-forming material was extracted with ether and worked up as described for the previous fractions. The product (31 g.) was a hard wax, m.p. 45–50°C. (Fraction III).

In an attempt to obtain more adduct-forming material, Fraction II was subjected to a second complexing operation similar to that applied to the lanolin. Three new fractions were obtained analogous to Fractions I, II, and III. The new fractions are designated as Fractions II A, II B, and II C in Table II. Fraction II A, although obtained in the same way as Fraction I, was not a fluid product at room temperature. Only an additional 2.2 g. (Fraction II C) of adduct-forming material was obtained from the second complexing reaction. The analyses of the frac-

TABLE I
Analyses of Fractions from Urea Fractionation

	Lanolin	Fraction I Fluid product	Fraction II Soxhlet extract	Fraction III Wax product (from adducts)
Weight (g.)	500.0	359.1	96.8	31.0
Acid No.	1.2	1.3	1.1	8.5
Saponification No.	96.6	94.5	84.4	85.8
% Hydroxyl	1.22	0.78	1.11	2.66
% Cholesterol ^a	19.4	19.3	21.8	1.1
% Triterpenoid sterols ^{a, b}	13.3	17.3	11.5	0.2

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² Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

^a Determined by the method of Luddy, Turner, and Scanlan (5).
^b Lanosterol, agnosterol, dihydrolanosterol and dihydroagnosterol.

tions and of the original lanolin are given in Table I. All of Fraction II was used in the second complexing operation to obtain Fractions II A, II B, and II C.

The analysis of Fraction III shows it to be a mixture of esters with a hydroxyl content greater than that of lanolin. The fact that it forms a urea adduct and has an insignificant sterol content suggests that these esters are aliphatic. It may be assumed that the material in Fraction II C is similar to that in Fraction III since it also forms a urea adduct.

TABLE II
Analyses of Fractions Obtained from Refractionation of Fraction II

	II A Cold ether extract	II B Soxhlet extract	II C Wax prod- uct (from adducts)
Weight (g.).....	64.6	21.1	2.2
Acid No.....	1.2	0.8
Saponification No.....	90.7	65.2
% Hydroxyl.....	1.14	1.04
% Cholesterol.....	20.8	24.9
% Triterpenoid sterols.....	14.3	3.0

As would be expected, acetylation of the fluid fraction decreased the viscosity of the sample. Viscosities at 25°C. as measured with a Fenske Modified Ostwald viscometer, were 32.5 stokes for the unacetylated material and 14.55 stokes for the acetylated product.

Hydrocarbon solvents, such as iso-octane and petroleum ether, were also used to extract the nonadduct-forming material from the urea complexes. The products obtained were similar to those when ether was used. The yields were about the same, but the viscosity of the fluid fraction was somewhat higher.

For purposes of comparison there are included analytical data on both a fluid fraction and a solid fraction that were obtained from a solvent fractionation of lanolin (4). In this method the fluid fraction comprises that portion of lanolin which remains in solution when a 20% solution of lanolin in isopropyl alcohol is maintained at 5°C. for approximately 16 hr. The analytical data on the fluid and hard-wax fractions obtained by urea fractionation and similar data on the two products from solvent fractionation are compared in Table III.

TABLE III
Comparison of Fractions from Urea and Solvent Preparations

	Lan- olin	Fluid fractions		Solid fractions	
		Urea separa- tion	Solvent separa- tion	Urea separa- tion	Solvent separa- tion
Weight, %.....	71.0	40.0	6.0	60.0
Acid No.....	1.2	1.3	2.7	8.5	0.0
Saponification No.....	96.6	94.5	93.2	85.8	92.4
Hydroxyl, %.....	1.22	0.78	1.17	2.66	0.86
Cholesterol, %.....	19.4	19.3	14.9	1.1	22.0
Triterpenoid sterols, %.....	13.3	17.3	20.9	0.2	11.1
Viscosity, stokes (25°C.).....	32.5	24.6

When the analyses of the two fluid fractions are examined, wide differences in yield and sterol content are apparent. In urea separation the yield of fluid fraction is about 71%, and two-thirds of the cholesterol originally present is found in this fraction. In solvent fractionation the fluid fraction constitutes only 40% of the original material and contains less than one-third of the cholesterol originally present.

The differences in sterol content are even more noticeable when one compares the analysis of the hard-wax fraction obtained from the decomposition of the urea complexes with that of the solid fraction from solvent separation. The total sterol content of the solvent-derived product is about the same as that in the fluid fractions, and the cholesterol content is about twice the triterpenoid-sterol content. The solid fraction from urea separation contains practically no sterols. The absence of sterols demonstrates conclusively the specificity of the urea-complexing reaction. The physical nature of the two solid fractions is also different. The product from the solvent separation is a soft grease. The solid from the urea complexes is a hard wax.

Summary

A fractionation of lanolin was effected by contacting lanolin with urea in the presence of methyl alcohol. About 6-8% of the lanolin formed a urea adduct which, upon decomposition, yielded a hard, nontacky wax fraction. In addition to the wax fraction, a fluid fraction and a sticky semi-solid were also obtained. The latter two fractions were obtained by the solvent extraction of the nonadduct-forming material from the urea adducts.

The fluid fraction, obtained in 71% yield, is a viscous liquid at room temperature. The fluid properties of the fraction can be improved by acetylation.

REFERENCES

1. Conrad, L. I., and Motiuk, K., *Am. Perfumer Aromat.*, **67**, No. 4, 35-9, 48 (1956); U. S. Patent 2,725,334, November 29, 1955.
2. Horn, D. H. S., Hougden, F. W., von Rudloff, E., and Sutton, D. A., *J. Chem. Soc.*, **1954**, 177-180.
3. Horn, D. H. S., and Hougden, F. W., *Chemistry and Industry*, **1951**, 670; *J. Chem. Soc.*, **1953**, 3533-3538.
4. Le Compte, G. C., and Ault, W. C., U. S. Patent 2,735,780, February 21, 1956.
5. Luddy, F. E., Turner, Arthur Jr., and Scanlan, John T., *Anal. Chem.*, **25**, 1497-1499 (1953); *ibid.* **26**, 491 (1954).
6. Murray, K. E., and Schoenfeld, R., *J. Am. Oil Chemists' Soc.*, **29**, 416-420 (1952).
7. Tiedt, J., and Truter, E. V., *J. Chem. Soc.*, **1952**, 4628-4630.
8. Truter, E. V., *J. Chem. Soc.*, **1951**, 2416-2419; *Research* **6**, 320-326 (1953).
9. Truter, E. V., *Quarterly Reviews*, **5**, 390-404 (1951); see also "Wool Wax, Chemistry and Technology," p. 55, Interscience Publishers Inc., New York (1956).
10. Weitkamp, A. W., *J. Am. Chem. Soc.*, **67**, 447-454 (1945).